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## Development of oxygen sensor for pyrochemical reactors of spent nuclear fuel reprocessing

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**Abstract.** The problem of closing the nuclear fuel cycle is not only related to the development of new types of nuclear fuel and the operation of fast neutron reactors, but also to the complex schemes for the pyrochemical reprocessing of spent nuclear fuel (SNF), which, in turn, require adherence to strict process parameters. In particular, this concerns the operation of the reduction of oxidized SNF mainly by metallic lithium. The paper presents the basic scientific principles and the results of experimental verification of the operation of an electrochemical sensor for measuring oxygen in molten salts in pyrochemical reactors for the reprocessing of spent nuclear fuel. The sensor design consists of two combined electrochemical cells based on the solid electrolyte  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  with a common reference electrode. The sensor allows continuous measurement of the oxygen activity in the oxide-chloride melt and the partial pressure of oxygen in the gas atmosphere above the melt directly during the process of pyrochemical processing. Experimental verification of the sensor performance was performed in a reactor with  $\text{LiCl-Li}_2\text{O}$  melts at a temperature of 650 °C. The resource of continuous sensor operation exceeded 500 hours, and the number of thermal cycles without destruction was at least 20. The sensor readings were found to depend on the specified  $\text{Li}_2\text{O}$  content in the  $\text{LiCl}$  melt.

### 1. Introduction

Currently, in a number of countries, complex schemes are being developed for the pyrochemical processing of SNF, including a number of technological operations in reactors with molten salts and strictly controlled inert atmosphere [1-3]; the efficiency and technological parameters of this operation are largely determined by the oxygen content of the salt melt and the partial pressure of oxygen above the melt. It is worth noting that in the case of the reduction of oxidized SNF, the control and maintenance of a given concentration of oxygen ions in the melt in a certain range are necessary. When performing other operations (electrorefining, chlorination), the presence of oxygen in chloride melts is extremely undesirable and therefore control of oxygen content is also necessary.



To control the oxygen content directly in reactors with oxide-chloride melts, electrochemical sensors on solid electrolytes seem to be the most promising [4]. This paper demonstrates the basic principles of operation and presents an experimental verification of the performance of an electrochemical sensor with two electrochemical cells for measuring the oxygen content of a LiCl-Li<sub>2</sub>O melt and the atmosphere above it in a laboratory reactor at 650 °C.

## 2. The scheme and principle of operation of the oxygen control sensor

The proposed electrochemical sensor consists of two combined electrochemical cells based on an oxygen-conducting solid electrolyte with a composition of 0.9ZrO<sub>2</sub> - 0.1Y<sub>2</sub>O<sub>3</sub> (YSZ) with a common reference electrode. The YSZ electrolyte is selective in oxygen and has an ion transfer number of 1. Studies by a number of foreign authors [1-2] showed rather good chemical and erosion resistance of YSZ samples in the studied melts.

The solid sensor electrolyte was made in the form of a thin-walled test tube with a diameter of 10 mm and a height of 150 mm. The reference electrode of the Ni-NiO composition was placed inside the tube, and the same electrode provided a stable value of the partial pressure of oxygen at a constant temperature. Figure 1 shows a diagram of the sensor device and a general view of an experimental sample sensor for testing. Measuring platinum electrodes deposited on the outer surface of the tube. To remove the oxygen potential of the molten salt, one of the measuring electrodes was deposited on the end of the tube, and the second measuring electrode, designed to remove the potential of the gas atmosphere, was deposited at a height of 110 mm from the end of the tube. During measurements, the device is placed in the reactor so that the lower measuring electrode is immersed in the analyzed melt, and the second measuring electrode is washed by the gas atmosphere. [5].

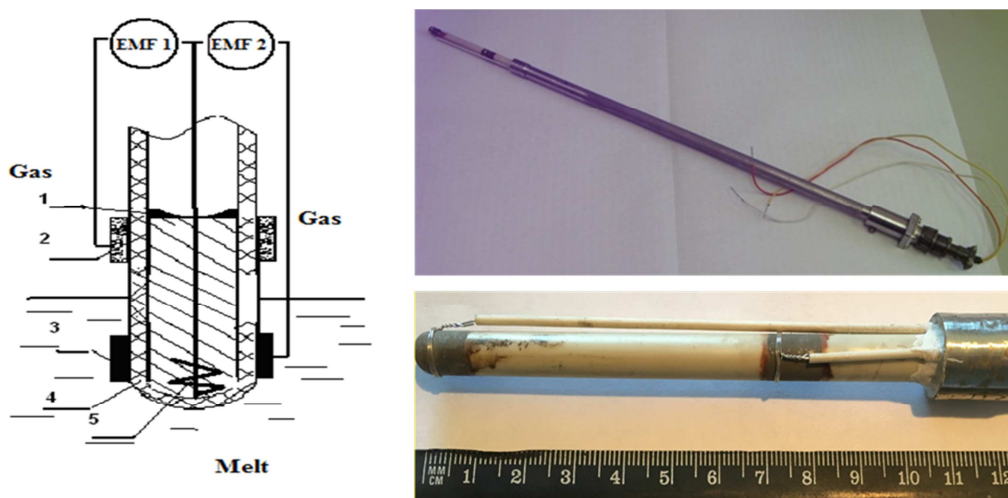
The principle of the sensor operation is to measure the potential difference between the common reference electrode and each of the measuring electrodes.

## 3. Experimental methods in the melt LiCl-Li<sub>2</sub>O and test results

Experimental testing of the sensor was carried out in a laboratory reactor, being a quartz tube with a glass carbon crucible installed at the bottom. LiCl salt was placed in a glassy carbon crucible. The test tube was sealed using a fluoroplast cap with openings for the sensor, gas feed-outlet, thermocouple, and loading of Li<sub>2</sub>O oxide and brought to the experimental temperature (650 °C). To avoid thermal shocks, the sensor was heated directly in the reactor.

When the working temperature was reached, the sensor was immersed in the melt and the registration of the values of the EMF (electromotive force) 1 and EMF (electromotive force) 2 of the sensor began. For fixing the values the device PGSAT AutoLab 302N was used (The MetrOhm, Netherlands). During the measurements, premeasured amounts of Li<sub>2</sub>O were added to the melt and samples of the melt were taken for chemical analysis.

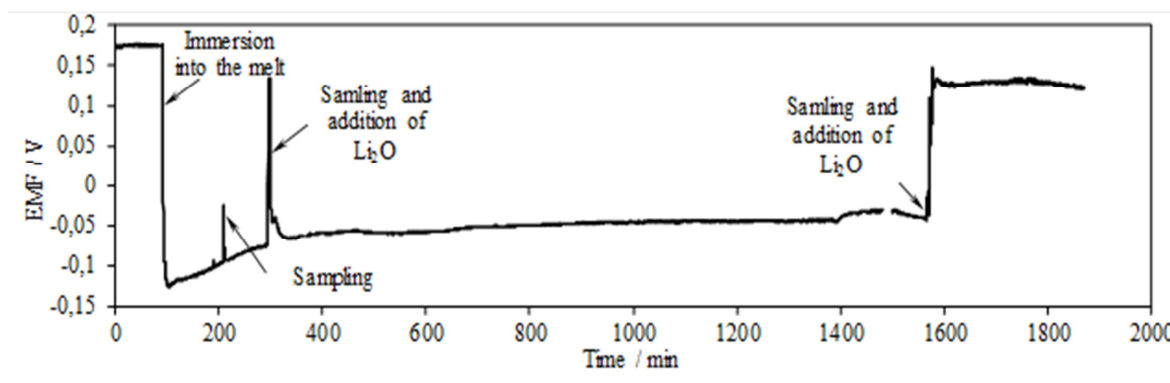
Within an hour, the sensor was heated in an argon atmosphere. To create an atmosphere, high-purity first-grade argon was used, and additional purification from moisture was carried out.



**Figure 1.** Scheme and photos of electrochemical oxygen sensor:

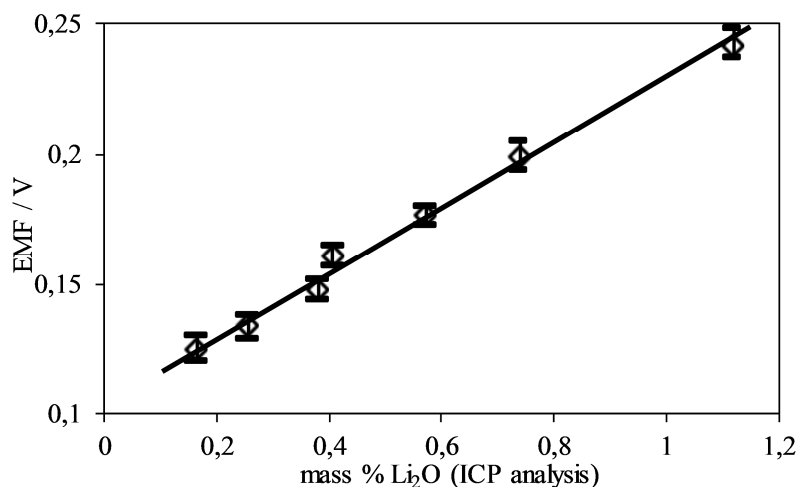
1 – Sealant; 2 – Outer electrode (Pt) in the gas phase; 3 – Outer electrode (Pt) in the melt under study; 4 – solid – electrolyte tube (YSZ); 5 – Reference inner electrode (Ni – NiO); EMF 1 and EMF 2 – potentiometers.

Within one hour, the sensor measured the partial pressure of oxygen in argon. The values of EMF1 and EMF2 were  $0.17 \pm 0.005$  V, which corresponds to the oxygen content of  $1.13 \times 10^{-12}$  at.%. At 92 minutes, the sensor was immersed in the melt, to a depth of 40 mm. Figure 2 shows the decrease of the EMF2 of the sensor to -0.12 V, after which the value of the EMF2 slowly increased to -0.07 V. The sufficiently long stabilization time is associated with the establishment of an equilibrium oxygen potential at the measuring electrode.



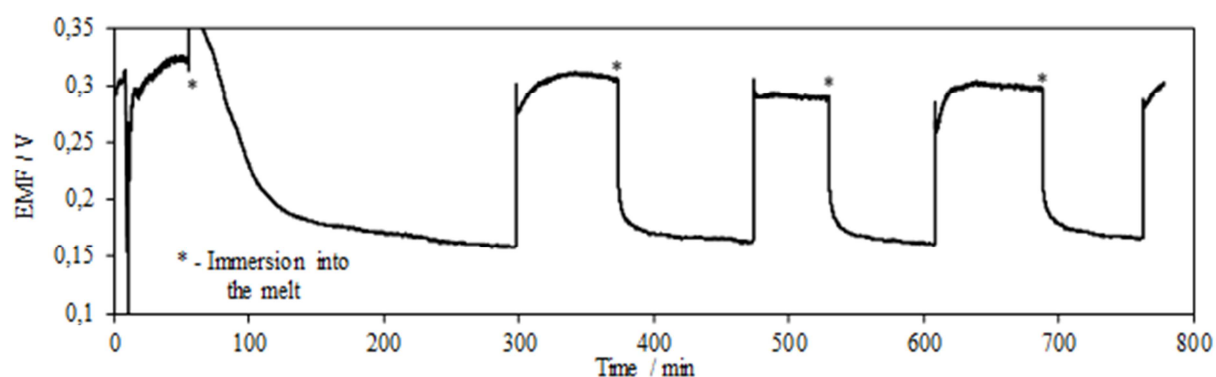
**Figure 2.** Changing the potential of the oxygen sensor in the melt LiCl-Li<sub>2</sub>O.

After adding 0.05% wt.% Li<sub>2</sub>O to the LiCl melt, the EMF 2 value began to grow and stabilized in the range of values from -0.05 to 0.06 V. After 22 hours, the sensor was kept in the melt and the next load of Li<sub>2</sub>O was 0.2 wt.% to the melt at 1580 minute. The EMF 2 sensor again shifted to the positive area and stabilized at a value of about 0.125 V for 10-12 minutes, after which significant deviations and fluctuations of the EMF 2 values were not observed during the day. From the data obtained, it can be concluded that the EMF 2 sensor responds to the content of Li<sub>2</sub>O in the melt and this value is stable with each addition of Li<sub>2</sub>O.



**Figure 3.** Dependence of EMF2 on the concentration of Li<sub>2</sub>O in the LiCl-Li<sub>2</sub>O melt at 650 °C.

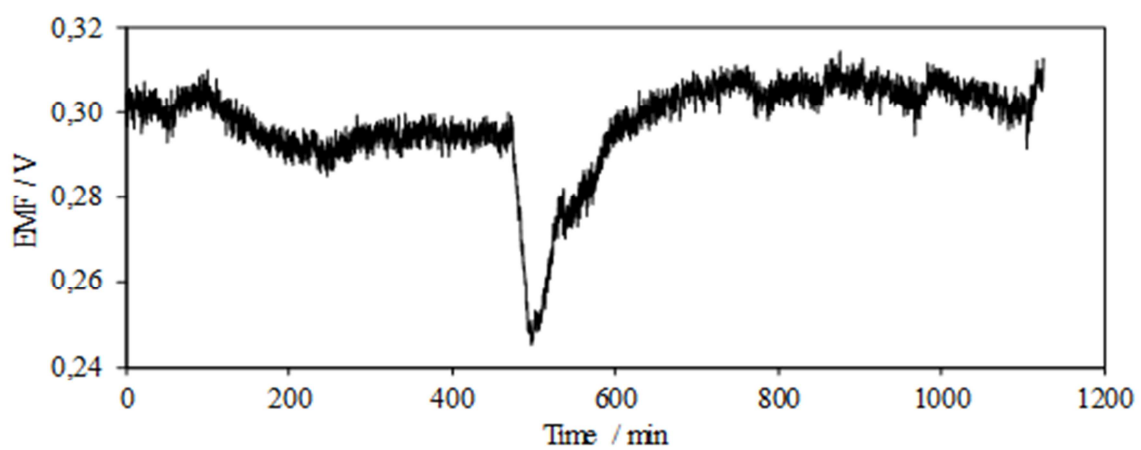
From figure 3 it can be concluded that the dependence of the oxygen sensor EMF 2 on the content of Li<sub>2</sub>O oxide is linear. Consequently, the concentration of Li<sub>2</sub>O in the melts of pyrochemical processing of SNF with high accuracy can be determined directly in the reactor by the obtained calibration dependence.



**Figure 4.** The change of the readings (EMF) of the oxygen sensor in molten LiCl-Li<sub>2</sub>O at periodic immersion in the melt.

The performance of the sensor was tested during its short-term immersion in the melt (figure 4). After immersion in the melt, the sensor was held until a stable value of the potential was established. Then the sensor was taken out of the melt, kept in the atmosphere above the melt, and the cycle repeated again. It is seen that the sensor EMF2 is well and quickly reproduced, and the deviation of its values from the average does not exceed  $\pm 0.005$  V. According to the data obtained, it is also possible to estimate the dynamic capabilities of the sensor in the analysis of oxygen activity in the salt melt. The response time is from 1 to 10 seconds, and the signal output at 90% of the nominal value is not more than 10 minutes.

During the period of the test sensor for measuring oxygen activity in the melt was carried out the readings of the sensor for measuring the partial pressure of oxygen in the gas phase above the melt. EMF 1 of the sensor in the gas phase was quickly installed and practically did not change (figure 5) except for the moments of sampling and loading into the melt of the next portions of Li<sub>2</sub>O.



**Figure 5.** The change in potential of the oxygen sensor in the atmosphere above the LiCl-Li<sub>2</sub>O melt (EMF1) at the time of Li<sub>2</sub>O loading

During measurements, the EMF 1 of the oxygen sensor above the LiCl-Li<sub>2</sub>O melt increased with the growth in the content of Li<sub>2</sub>O in the melt and at 1.12 wt.% oxide was about 0.3 V, which corresponds to the concentration of oxygen in argon at  $7.8 \cdot 10^{-10}$  at.%. Changes in EMF 1 sensor are associated with the attempt of extraction and introduction of attachments in Li<sub>2</sub>O, when the cell could get some uncontrolled amount of oxygen. However, after the sampling procedure or introduction of the Li<sub>2</sub>O sample, the EMF 1 value of the sensor returned to 0.3 V, which indicates a relatively rapid relaxation of the atmosphere above the melt. While the EMF 1 value of the oxygen sensor above the melt can be an indicator of the serviceability of the device, since a sharp change in the readings will signal a technological or instrumental violation in the operation of the device.

Figure 6 shows the sensor after a long exposure in the LiCl-Li<sub>2</sub>O melt; the test duration was 500 hours, with the device standing more than 20 heat changes.



**Figure 6.** Appearance of the device with potentiometric sensors after measurements for 500 h in the melt LiCl-Li<sub>2</sub>O.

#### 4. Conclusion

The tests have shown that the oxygen sensor in the LiCl-Li<sub>2</sub>O melt reacts to changes in the concentration of Li<sub>2</sub>O oxide, while in the measured range the dependence of the EMF 2 sensor on the content of Li<sub>2</sub>O is linear and reproducible. The sensor has shown operability and good reproducibility of the measurement results both in conditions of constant presence in the melt and during periodic immersion in the melt.

Control of the partial pressure of oxygen in the atmosphere over the melt has shown that the composition of the atmosphere over the melt with a constant content of Li<sub>2</sub>O is stable, while an

increase in the oxide content in the melt increases the oxygen content in the atmosphere above the melt.

In general, the proposed sensor has been experimentally tested and proved good performance for 500 hours at 20 heat shifts. This indicates the possibility of its use to control pyrochemical processes of SNF processing.

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